

HARD ALLOY AND W-BASED COMPOSITE CARBIDE POWDER USED AS STARTING MATERIAL

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BACKGROUND OF THE INVENTION

1. Field of the invention

10 The present invention relates to a hard alloy to be used for cutting tools, wear resistant tools, corrosion resistant and wear resistant parts, etc., and particularly to a hard alloy in which characteristics such as hardness, toughness, strength, wear resistance, fracture resistance, plastic deformation resistance, thermal crack resistance, 15 antioxidation property, corrosion resistance, etc., by adding specific element(s) to crystal of hexagonal tungsten carbide which is a primary hard phase as a solid solution, and to a W-based composite carbide powder which becomes a starting material thereof.

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2. Prior art

A hard alloy produced by mixing, in addition to WC and Co, other powder of carbides such as TiC, TaC, VC, Cr₃C₂, etc., 25 subjecting to molding under pressure, and sintering under heating has been used for various kinds of uses such as cutting tools, wear resistant tools and parts. Also, by adjusting grain size of WC, a Co amount, a kind and amount of a carbide to be added, and the like, alloy characteristics such as hardness, strength, toughness, heat resist- 30 ance, oxidation resistance, corrosion resistance, etc. required for the respective uses are obtained. With regard to the other carbides to be added, for example, TiC is added to steel cutting tools in which wear due to a 35 reaction or welding becomes a problem, TaC and/or ZrC is/are added to hot-working mold or steel cutting tools in

which plastic deformation at high temperatures becomes a problem, VC and/or Cr_3C_2 is/are added to a drill to which hardness and strength are required as a grain growth inhibitor of WC, and Cr_3C_2 and/or Mo_2C is/are added to wear resistant parts in which corrosion becomes a problem.

However, when one of the alloy characteristics is improved by adding another carbides, there is a problem of antinomy wherein the other alloy characteristics is lowered. For example, when TiC, TaC, ZrC or VC is added, strength or toughness is markedly lowered even when an amount thereof to be added is a little. Also, Cr_3C_2 improves corrosion resistance or oxidation resistance of a binder phase, but WC causes alkali corrosion or preferential oxidation, so that its effect cannot sufficiently be revealed.

As a measure of the above problems, it has been proposed powder (for example, Japanese Provisional Patent Publication No. Hei.7-54001, Japanese PCT Provisional Patent Publication No. 2000-512688, Japanese Provisional Patent Publications No. Hei.10-212165 and No. Hei.11-236221) for manufacture of a hard alloy to which other carbides are contained in WC powder, or a hard alloy (for example, Japanese Provisional Patent Publications No. Hei.10-298698, Hei.11-6025, 2001-81526 and Hei.10-45414) to which other metals such as Cr, Mn, Re, etc. have been added. The former is intended to prevent from lowering in strength, toughness, etc., while maintaining added effects of the other carbides by dispersing the fine other carbides uniformly, and the latter is intended to strengthen a binder phase by alloying other metals.

Among the prior art references which relate to powder for producing a hard alloy containing other carbides, in Japanese Provisional Patent Publication No. 7-54001, there is disclosed a preparation method of fine complex carbide

powder for preparation of a tungsten carbide-based hard alloy in which mixed powder comprising tungsten oxide, cobalt oxide, carbon, and further carbides of V, Cr, Ta and/or Nb each having an average particle diameter of about 1 μm or lower is subjected to reduction treatment and carbonization treatment both at 700 to 1200°C. In Japanese PCT Provisional Patent Publication No. 2000-512688, there are disclosed powder comprising a transition metal carbide and Group VIII metal and a process for preparing the same, which comprises heating a precursor mixed powder which becomes a metal selected from iron, cobalt and nickel and a transition metal carbide of a metal selected from tungsten, titanium, tantalum, molybdenum, zirconium, hafnium, vanadium, niobium and chromium at 1173 to 1773K (900 to 1500°C). In Japanese Provisional Patent Publication No. 10-212165, there are disclosed a complex carbide containing a tungsten carbide obtained by heating a mixed powder comprising tungsten oxide and chromium oxide or metallic chromium in hydrogen atmosphere at 700 to 1100°C to obtain a solid solution or a intermetallic compound, mixing carbon powder thereto, and carbonizing in hydrogen and vacuum at a temperature of 1300 to 1700°C, and 0.5 to 2.0% by weight of metal chromium based on the amount of the tungsten carbide, and a process for preparing the same.

In complex carbide powders comprising tungsten carbide and transition metal, transition metal carbide, iron-group metal and the like described in these references, transition metal or its carbide is uniformly and finely dispersed, so that when they are used as a hard alloy, characteristics such as hardness, strength, toughness, etc. can be improved but a heating temperature is low so that an amount of the transition metal dissolved in tungsten carbide is extremely little, whereby there is no improvement in characteristics of the tungsten carbide itself. Thus, there is a problem that an antinomy problem possessed by

the hard alloy cannot be solved.

Also, in Japanese Provisional Patent Publication No. Hei. 11-236221, there is disclosed a complex carbonitride material comprising high melting point metals represented by the formula: $(M_1m, M_2n)(C_xN_y)$ wherein M_1 and M_2 are each metal element having a high melting point different from each other among Nb, Mo, Ta and W, $m+n=1$, $0 < m < 1$, $x+y \approx 1$, $x \leq 0.99$ and $y \geq 0.01$, particularly to $(W, Mo)(CN)$. This is to subject a $(W, Mo)C$ solid solution which has conventionally been well known to nitriding synthesis by heating to 500 to 2000°C in a nitrogen atmosphere at a pressure of 10 atm or higher. The $(W, Mo)(CN)$ powder disclosed in this publication has a wide range of an amount of Mo as a solid solution and when it is employed for a hard alloy, an effect of making particles fine by the nitrogen can be expected. However, when an amount of Mo to be dissolved as a solid solution is large, there are problems that decreases in hardness, strength, wear resistance, plastic deformation property and oxidation resistance are remarkable.

Among the prior art references relating to hard alloys to which other metal(s) is/are added, in Japanese Provisional Patent Publication No. Hei.10-298698, there is disclosed a hard alloy comprising 3 to 25% by weight of Co and Ni, 0.1 to 3% by weight of chromium carbide based on the amount of Co and Ni, and the reminder being tungsten carbide and inevitable impurities, and in Japanese Provisional Patent Publication No. Hei.11-6025, there are disclosed a hard alloy comprising 3 to 25% by weight of Co and Ni in total, 10 to 30% by weight of Cr in terms of chromium carbide based on the amount of Co and Ni, and the reminder being tungsten carbide and inevitable impurities, a coated alloy using the hard alloy as a matrix and coated cutting tools.

In these chromium-containing hard alloys disclosed in both

of the publications, a Cr content, a Co/Ni ratio and grain size of WC are limited to optimum ranges when they are used as cutting tools, and Cr is dissolved in a metal binder phase, but is not dissolved in WC as a solid solution, so
5 that there is a problem that an effect of Cr added cannot sufficiently be shown.

Also, in Japanese Provisional Patent Publication No. 2001-81526, there is disclosed an iron-based hard alloy comprising a binder phase which comprises Fe containing 0.35
10 to 3.0% by weight of C, 3.0 to 30.0% by weight of Mn, and 3.0 to 25.0% by weight of Cr. In Japanese Provisional Patent Publication No. Hei.10-45414, there is disclosed a hard alloy using titanium compound powder as a starting
15 material, which powder has a coated film on the surface thereof, comprising at least one substance selected from the group consisting of Groups 4a, 5a, 6a metal except for titanium, their carbide, nitride and carbonitride, and rhenium metal and iridium metal.

20 The hard alloys containing Mn or Re metal disclosed in these publications are to improve strength, toughness, corrosion resistance, heat resistance, etc. of the hard alloy by adding these metals as a solid solution to a metal
25 binder phase, but these metals are not dissolved in WC, so that an effect of adding Mn or Re is little and if an amount of these metals to be added is large, the metal binder phase becomes brittle whereby there are problems that strength and toughness are lowered.

30 The present invention is to solve the above-mentioned problems, and specifically, an object of the present invention is to provide a hard alloy in which contradicting alloy characteristics of the hard alloy are simultaneously
35 improved by dissolving specific element(s) such as Ti, Zr, V, Ta, Cr, Mn, etc. into crystalline of WC as a solid

solution whereby hardness, toughness, oxidation resistance, corrosion resistance, etc. of the WC itself are improved, and to provide W-based composite carbide powder which becomes a starting material of the hard alloy.

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SUMMARY OF THE INVENTION

The present inventors have studied to improve contradicting characteristics of hard alloy at the same time for a long
10 period of time, and as a result, they have found that to improve characteristics of WC itself is effective, various characteristics of the alloy can be improved when specific element(s) is/are dissolved in the crystal of WC, metals belonging to Group IVB (Ti, Zr, Hf), VB (V, Nb, Ta) or VIB
15 (Cr, Mo) of the Periodic Table (except for W), and Mn and Re are the most effective as the specific element(s), and WC dissolved the specific element(s) therein can be obtained by subjecting a mixed powder of W, C and an oxide of the specific element(s) to heat treatment, whereby they
20 have accomplished the present invention.

That is, the hard alloy of the present invention comprises 5 to 50% by volume of a metallic binder phase comprising at least one element selected from cobalt, nickel and iron as
25 a main component, 0 to 40% by volume of a cubic crystal compound comprising at least one compound selected from a carbide, nitride and mutual solid solution of a metal of Group IVB (Ti, Zr, Hf), VB (V, Nb, Ta), VIB (Cr, Mo) of the Periodic Table, and the reminder being hexagonal tungsten
30 carbide and inevitable impurities, wherein at least one specific element(s) selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, manganese and rhenium is dissolved in the crystal of the hexagonal tungsten carbide as a solid
35 solution in an amount of 0.1 to 3.0% by weight based on the amount of the tungsten carbide.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The hexagonal tungsten carbide in the hard alloy of the present invention is a material in which at least one of the specific element(s) selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn and Re is dissolved in the crystal of WC as a solid solution. More specifically, there may be mentioned (W,Ti)C, (W,Zr)C, (W,V)C, (W,Ta)C, (W,Cr)C, (W,Mo)C, (W,Re)C, (W,Ti,Mo)C, (W,Zr,Cr)C, (W,V,Cr)C, (W,Nb,Mn)C and (W,Ta,Re)C, which are a complex carbide having the same hexagonal structure as that of WC. An amount of the specific element(s) to be dissolved in WC as a solid solution is defined to be 0.1 to 3.0% by weight, since if it is added in an amount of less than 0.1% by weight, improved effects in hardness, toughness, oxidation resistance, corrosion resistance, etc. are little, whereas Ti, Zr, Hf, V, Nb or Ta is extremely difficult to be dissolved in WC in an amount exceeding 3.0% by weight, and even when Cr, Mo, Mn or Re can be dissolved in WC in an amount exceeding 3.0% by weight, it accompanies with lowering in hardness or oxidation resistance, or formation of brittle sub-carbide material. The amount is preferably 0.3 to 2% by weight.

Here, the specific element(s) dissolved in WC crystal has slightly different characteristics to be provided to the hard alloy depending on the kind thereof. For example, Ti, Zr, Hf and V improve hardness, wear resistance, welding resistance, oxidation resistance, etc., Nb and Ta improve toughness, fracture resistance, heat resistance, etc., Cr improves toughness, oxidation resistance and corrosion resistance, and Mo, Mn and Re improve hardness, toughness, heat resistance, etc.

In the hard alloy of the present invention, it is preferred

that the specific element(s) is/are at least one selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium and tantalum, and a content of a cubic crystal compound mentioned hereinbelow is 1% by volume or less, since strength and toughness are particularly high. Also, it is preferred that the specific element(s) is chromium, and 0.1 to 10% by weight of chromium is contained based on the total amount of the hard alloy, since chromium is also dissolved in the metal binder phase as a solid solution, so that improved effects of hardness, toughness, heat resistance, corrosion resistance, oxidation resistance, etc. are more remarkable. Moreover, it is preferred that the specific element(s) is/are manganese and/or rhenium, and 0.1 to 10% by weight of manganese and/or rhenium is/are contained in the total amount of the hard alloy, since it is/they are also dissolved in the binder phase, whereby improved effects of hardness, toughness, heat resistance, etc. are more remarkable.

The metal binder phase of the hard alloy according to the present invention comprises an alloy containing iron group metal (Fe, Co, Ni) as a main component and 30% by weight or less of W is dissolved therein. More specifically, the binder phase may be mentioned, for example, Co-W alloy, Co-Re alloy, Co-W-Cr alloy, Ni-Mo alloy, Ni-Cr-W alloy, Co-Ni-Cr-W alloy, Fe-Ni-W alloy, Fe-Mo-Cr alloy, Fe-Mn alloy, and the like. An amount of the metal binder phase is defined to be 5 to 50% by volume, since if it is less than 5% by volume, micro pores are remained in the alloy, so that hardness, strength, toughness or fracture resistance is lowered, while if it exceeds 50% by volume, hardness or wear resistance is lowered.

The cubic crystal compound which is an optional component of the hard alloy according to the present invention may be specifically mentioned, for example, VC, NbC, TaC, (W,Ti)C,

(W,Zr)C, (W,Ti,Ta)C, (W,Ti,Re)C, TiN, ZrN, HfN, (W,Ti,Ta)-(C,N), (W,Ti,Mo)(C,N), and the like. Here, the hard alloy of the present invention may contain Cr_7C_3 , Mo_2C , etc. which do not belong to the cubic crystal compound with a small amount. If the content of the cubic crystal compound in the hard alloy exceeds 40% by volume, an amount of WC to which the specific element(s) is/are dissolved is relatively lowered, so that an improved effect thereof becomes a little.

For preparing the hard alloy of the present invention, it is necessary to use powder in which the specific element(s) has/have previously been dissolved in the WC crystal as a starting material. That is, the W-based composite carbide powder of the present invention comprises complex carbide powder which contains tungsten, carbon, and at least one specific element(s) selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, manganese and rhenium, wherein said complex carbide powder contains 80% by volume or more of hexagonal tungsten carbide, and 0.1 to 3.0% by weight of the specific element(s) is/are dissolved in the crystals of the hexagonal tungsten carbide.

An amount of the specific element(s) to be dissolved in the W-based composite carbide powder of the present invention is defined to be 0.1 to 3.0% by weight, since if it is less than 0.1% by weight, improved effects on the WC itself such as hardness, toughness, oxidation resistance, corrosion resistance, etc. are low, and it is difficult to dissolve the specific element(s) in an amount exceeding 3.0% by weight in the WC crystal. Here, when the complex carbide of the present invention is represented by the chemical formula, it is a material of $(\text{W}_{1-x}\text{M}_x)\text{C}_y$ wherein x and y satisfy the relationship of $0.002 \leq x \leq 0.06$ and $0.95 \leq y \leq 1.00$ since the specific element(s) is/are substituted for the W

atom in the WC crystal, and taken into the hexagonal crystal lattice. Provided that M represents at least one of the specific elements.

- 5 The W-based composite carbide powder of the present invention comprises WC in which the specific element(s) is/are dissolved as a main component, and a cubic crystal compound into which W is dissolved, and W_2C , Cr_3C_2 , Mo_2C or the like into which the specific element(s) is dissolved.
- 10 If an amount of the WC in which the specific element(s) is/are dissolved is less than 80% by volume, improved effects on hardness, toughness, oxidation resistance, corrosion resistance, etc. due to the specific element(s) dissolved in WC are little in the hard alloy to be produced
- 15 by using the present products.

Here, the cubic crystal compound which may be contained in the complex carbide powder comprises W, carbon and/or nitrogen, and at least one selected from the group

20 consisting of titanium, zirconium, hafnium, vanadium, niobium and tantalum. Specific compositions thereof may be mentioned $(W_{0.6}Ti_{0.4})Co_{0.8}$, $(W_{0.06}Zr_{0.95})Co_{0.75}$, $(W_{0.45}V_{0.55})Co_{0.9}$, $(W_{0.65}Ta_{0.35})Co_{0.9}$, $(W_{0.5}Ti_{0.5})(Co_{0.9}No_{0.1})_{0.95}$, $(W_{0.5}Ti_{0.3}Ta_{0.2})Co_{0.9}$, and the like. These cubic crystal compounds are formed when

25 the specific element(s) is/are added exceeding a limit of an amount capable of being dissolved, and to show added effects of the specific element(s) at the highest level, the presence of the cubic crystal compound is sometimes preferred. However, if an amount thereof becomes 20% by

30 volume or more, it becomes difficult to adjust a ratio of the composition for producing the hard alloy, and in particular, a problem of lowering in strength of the hard alloy arises. Also, W_2C is likely formed when the content of carbon is lower, when the powder is subjected to heat

35 treatment at higher temperatures, when the specific element(s) is Cr or Mo, or the like, but to enlarge an

amount of the element(s) to be dissolved, W_2C is rather preferably contained in an amount of up to 5% by volume.

In the W-based composite carbide powder of the present invention, it is preferred that the WC crystal to which the specific element(s) is/are dissolved has a lattice constant of a axis of a hexagonal crystal lattice of 0.2910 nm or longer and/or a lattice constant of c axis of the same of 0.2840 nm or longer, since dissolution of the specific element(s) in the WC crystal is complete and uniform whereby improved effects of the various kinds of characteristics become maximum.

The hard alloy of the present invention can be produced by the conventionally employed powder metallurgy method when the W-based composite carbide powder of the present invention is used as a starting material. On the other hand, the W-based composite carbide powder can be obtained, for example, by heating a mixed powder of WC and TiH_2 , a mixed powder of W, TiN and carbon, a mixed powder of WO_3 , TiO_2 and carbon and the like in a non-oxidative atmosphere or a combined atmosphere of reducing and carburizing atmospheres at high temperatures. Also, when it is produced by the following method and conditions, powder with a much amount of dissolution as well as a uniform dissolution degree and uniform grain size distribution can be produced.

That is, the W-based composite carbide powder of the present invention can be produced by subjecting a mixed powder comprising W powder, carbon powder and oxide powder of the specific element(s) each having a grain size of 1 μm or less to heat treatment at 1500 to 2000°C or so in an inert gas atmosphere or under vacuum. When the heat treatment temperature is higher, an amount of the specific element(s) dissolved in the powder increases but the WC crystals become coarse to cause abnormal grain growth. Also, when

Cr or Mn which has a higher vapor pressure is used as the specific element(s), it is necessary to carry out the procedure at a low temperature treatment in which an inert gas is introduced and dissipation thereof shall be prevented.

In the hard alloy of the present invention, the hexagonal tungsten carbide into which the specific element(s) is/are dissolved, which is in the W-based composite carbide powder used as a starting material has functions of improving hardness, toughness, heat resistance, corrosion resistance, oxidation resistance, etc. of the tungsten carbide itself, and the improved characteristics have functions of improving alloy characteristics or practical characteristics.

Example 1

By using each powder of commercially available W having an average particle size of 0.5 μm , carbon black (hereinafter referred to as "C") having an average particle size of 0.02 μm , TiO_2 , ZrO_2 , HfO_2 , V_2O_5 , Nb_2O_5 , Ta_2O_5 , Cr_2O_3 , MoO_3 and MnO_2 each having an average particle size of 0.05 to 0.2 μm , metal Re having an average particle size of 1.0 μm , and WC (hereinafter referred to as "WC/F") having an average particle size of 0.5 μm , TiC having an average particle size of 1.2 μm , Mo having an average particle size of 1.1 μm , WC (hereinafter referred to as "WC/C") having an average particle size of 3.5 μm , each powder was weighed with a formulation shown in Table 1, placed in a pot made of stainless steel with an acetone solvent and balls made of a hard alloy, mixed and pulverized for 24 hours and then dried to obtain respective mixed powders. Then, these mixed powders were each filled in a carbon crucible, and heated after inserting into a vacuum furnace. Heating was carried out under about 20 Pa vacuum until 1200°C, and

heating thereafter was carried out under atmosphere and a temperature shown in Table 1 maintaining for 1.0 hour to obtain products of the present invention (present products): PA to PR and Comparative product: complex carbide
5 powders of CA to CH. Provided that Comparative product: CH is not subjected to mixing and heat treatments.

Table 1

Sample No.	Composition (% by weight)	Heated atmosphere	Heated temperature (°C)	Results of X-ray diffractometry
Present products	PA 93.6W-6.2C-0.2TiO ₂	Vacuum about 10Pa	1800	WC+W ₂ C
	PB 93.0W-6.3C-0.7TiO ₂	Vacuum about 10Pa	1800	WC
	PC 91.3W-6.7C-2.0TiO ₂	Vacuum about 10Pa	1900	WC+(W, Ti) C+W ₂ C
	PD 88.7W-7.3C-4.0TiO ₂	Vacuum about 10Pa	2000	WC+(W, Ti) C+W ₂ C
	PE 92.7W-6.3C-1.0ZrO ₂	Vacuum about 10Pa	1900	WC+W ₂ C
	PF 92.8W-6.2C-1.0HfO ₂	Vacuum about 10Pa	2000	WC+W ₂ C
	PG 92.5W-6.5C-1.0V ₂ O ₅	Vacuum about 10Pa	1800	WC
	PH 92.6W-6.4C-1.0Nb ₂ O ₅	Vacuum about 10Pa	1900	WC+W ₂ C
	PI 92.7W-6.3C-1.0Ta ₂ O ₅	Vacuum about 10Pa	1900	WC+W ₂ C
	PJ 89.0W-7.0C-2.0Ta ₂ O ₅ -2.0TiO ₂	Vacuum about 10Pa	2000	WC+(W, Ta, Ti) C+W ₂ C
	PK 91.4W-6.6C-2.0Cr ₂ O ₃	0.1MPa Ar	1800	WC+W ₂ C
	PL 92.6W-6.4C-1.0Cr ₂ O ₃	0.1MPa Ar	1850	WC
	PM 90.9W-6.6C-2.0Cr ₂ O ₃ -0.5Ta ₂ O ₅	0.1MPa Ar	1900	WC+(W, Cr) ₂ C
	PN 88.9W-7.1C-4.0MoO ₃	Vacuum about 10Pa	1800	WC+W ₂ C
	PO 92.0W-6.5C-1.5MnO ₂	10kPa Ar	1500	WC+(W, Mn) ₂ C
	PP 91.8W-6.6C-1.0MnO ₂ -0.5Ta ₂ O ₅	10kPa Ar	1550	WC
	PQ 92.8W-6.2C-1.0Re	Vacuum about 10Pa	1800	WC
	PR 91.1W-6.3C-2.0Re-0.6Cr ₂ O ₃	0.1MPa Ar	1800	WC

Table 1 (contd.)

Sample No.		Composition (% by weight)	Heated atmosphere	Heated temperature (°C)	Results of X-ray diffractometry
Comparative products	CA	93.8W-6.2C	Vacuum about 10Pa	1700	WC
	CB	100.0WC/F	Vacuum about 10Pa	1600	WC+W ₂ C
	CC	93.7W-6.2C-0.1TiO ₂	Vacuum about 10Pa	1750	WC
	CD	99.8WC/F-0.2TiC	Vacuum about 10Pa	1800	WC+(W, Ti) C+W ₂ C
	CE	81.2W-8.8C-10.0TiO ₂	Vacuum about 10Pa	1900	(W, Ti)C+WC+W ₂ C
	CF	88.0W-7.0C-5.0Cr ₂ O ₃	0.1MPa Ar	1800	WC+(W, Cr) ₂ C
	CG	89.0W-6.0C-5.0Mo	Vacuum about 10Pa	1800	WC+W ₂ C
	CH	100.0WC/C	—	—	WC

Complex carbide powders of the thus obtained Present
 5 products PA to PR and Comparative products CA to CH were
 crushed and pulverized, and passed through a sieve of 100
 mesh to prepare sample powders for evaluation. With regard
 to these samples, X-ray diffraction analysis (tube: Cu,
 tube voltage; 50 kV, tube current; 250 mA) was carried out
 10 and components in the powder were identified. The results
 are also shown in Table 1.

Next, to the respective sample powders was added 30% by
 weight of cupper powder (commercially available electro-
 15 lytic copper powder: 2.5 μm) and the mixture was mixed by
 using a mortar, and after molding by a mold with a pressure
 of 2 ton/cm², these samples were heated and sintered under
 vacuum at 1150°C for 20 minutes to obtain sample alloys for
 analyses. Then, these sample alloys were polished by
 20 diamond whetstone and subjected to lap processing with a
 diamond paste having an average particle size of 1 μm, and

then, applied to observation and analyses by an electric field radiation type scanning electron microscope.

First, presence and distribution of WC and particles other
5 than WC (W_2C , cubic crystal compound, etc.) were confirmed
by compositional image contrast and element mapping. With
regard to WC and cubic crystal compound, compositional
analyses were carried out by focusing electronic beam to
the center portion of a particle having a relatively large
10 size. Also, a content (% by volume) of the respective
particles constituting the respective sample powders was
obtained by photographs and an image treatment device.
These results are shown in Table 2. Moreover, average
particle sizes of WC, W_2C and cubic crystal compounds were
15 obtained. The results are shown in Table 3.

Table 2

Sample No.		Amount of dissolved element in WC (% by weight)	Composition of powder (% by volume)		
			WC	W ₂ C	Cubic crystal compound
Present products	PA	0.12Ti	99.0	1.0	0
	PB	0.42Ti	100.0	0	0
	PC	0.82Ti	93.2	2.6	4.2 (W _{0.6} Ti _{0.4})C
	PD	0.87Ti	80.3	3.4	16.3 (W _{0.6} Ti _{0.4})C
	PE	0.73Zr	98.4	1.6	0
	PF	0.85Hf	97.1	2.9	0
	PG	0.57V	100.0	0	0
	PH	0.70Nb	98.0	2.0	0
	PI	0.82Ta	99.0	1.0	0
	PJ	0.80Ta+0.54Ti	86.8	3.2	10.0 (W _{0.6} Ta _{0.2} Ti _{0.2})C
	PK	1.37Cr	97.6	2.4	0
	PL	0.60Cr	100.0	0	0
	PM	1.00Cr+0.42Ta	99.0	1.0	0
	PN	2.73Mo	96.0	4.0	0
	PO	0.87Mn	98.7	1.3	0
	PP	0.62Mn+0.37Ta	100.0	0	0
	PQ	1.00Re	100.0	0	0
	PR	1.75Re+0.35Cr	100.0	0	0
Comparative products	CA	0	100.0	0	0
	CB	0	97.9	2.1	0
	CC	0.06Ti	100.0	0	0
	CD	0.08Ti	98.7	0.4	0.9 (W _{0.6} Ti _{0.4})C
	CE	0.85Ti	39.9	10.4	49.7 (W _{0.6} Ti _{0.4})C
	CF	3.22Cr	92.6	7.4	0
	CG	5.00Mo	90.9	9.1	0
	CH	0	100.0	0	0

Table 3

Sample No.		Average particle size (μm)			Lattice constants (nm)	
		WC	W ₂ C	Cubic system compound	a axis	c axis
Present products	PA	3.1	0.8	—	0.2913	0.2845
	PB	2.5	0.6	—	0.2911	0.2844
	PC	2.7	0.9	0.9	0.2917	0.2851
	PD	3.6	1.3	2.4	0.2915	0.2850
	PE	3.0	0.8	—	0.2914	0.2849
	PF	7.3	2.0	—	0.2913	0.2846
	PG	1.2	0.5	—	0.2911	0.2841
	PH	1.8	0.7	—	0.2912	0.2847
	PI	2.7	0.8	—	0.2916	0.2850
	PJ	3.5	1.1	2.2	0.2919	0.2852
	PK	3.1	2.2	—	0.2911	0.2847
	PL	2.0	—	—	0.2914	0.2847
	PM	2.4	1.5	—	0.2912	0.2844
	PN	2.4	2.9	—	0.2915	0.2849
	PO	2.5	1.8	—	0.2911	0.2850
	PP	2.4	—	—	0.2919	0.2841
	PQ	3.4	—	—	0.2914	0.2852
	PR	1.7	—	—	0.2919	0.2847
Comparative products	CA	3.1	0.8	—	0.2905	0.2837
	CB	1.3	0.9	—	0.2907	0.2835
	CC	2.9	0.8	—	0.2909	0.2841
	CD	3.2	1.7	1.4	0.2908	0.2839
	CE	2.8	0.8	1.8	0.2917	0.2852
	CF	2.2	2.4	—	0.2902	0.2831
	CG	3.2	1.4	—	0.2909	0.2855
	CH	3.5	1.1	—	0.2906	0.2837

Next, an interplanar spacing and a lattice spacing were

calculated from the position of a peak of WC ($2\theta=30$ to 120°) which was measured by the above-mentioned X-ray diffraction conditions, and lattice constants were obtained with respect to each of a axis and c axis by an
5 extrapolation method. The results are also shown in Table 3.

Example 2

10 By using complex carbide powders PA, PB, PE, PG, PH, PI, PJ, PK, PL, PM, PO, PP, PQ and PR as well as CA, CB, CD and CH obtained in Example 1, respective powders of W, C and metal Re used in Example 1, and commercially available Co having an average particle size of $1.0\ \mu\text{m}$, Ni with $1.2\ \mu\text{m}$,
15 Fe with $1.0\ \mu\text{m}$, metal Mn with $3.5\ \mu\text{m}$, and TiC, ZrC, VC, NbC, TaC and Cr_3C_2 each having 1.0 to $1.5\ \mu\text{m}$, these powders were weighed with a composition shown in Table 4, inserted in a pot made of stainless with an acetone solvent and balls made of hard alloy and pulverized and crushed for 48
20 hours, and then, dried to obtain respective mixed powders. Here, a formulated carbon amount was adjusted by addition of C or W, so that the alloy became medium carbon alloy (center of a range of a sound phase which does not precipitate free carbon or $\text{Co}_3\text{W}_3\text{C}$, $\text{Ni}_2\text{W}_4\text{C}$) after sintering. Then,
25 these powders were filled in a mold, and green compacts having a size of $5.5 \times 9.5 \times 29\ \text{mm}$ were produced with a pressure of $196\ \text{MPa}$, placed on a sheet comprising alumina and carbon fiber and heated by inserting into a vacuum atmosphere furnace. Up to 1200°C , the atmosphere was made
30 vacuum of about $20\ \text{Pa}$, and thereafter, heating was carried out in the atmosphere shown in Table 4, and sintering was carried out at 1400°C for 1.0 hour to obtain hard alloys of Present products 1 to 14 and Comparative products 1 to 14. Incidentally, Present product and Comparative product with
35 the same number were so formulated that the components of the hard alloy and grain size of WC are substantially the

same.

Table 4

Sample No.	Composition (% by weight)	Sintering atmosphere
Present products	1 93.0PA-7.0Co	Vacuum about 10Pa
	2 93.0PB-7.0Co	Vacuum about 10Pa
	3 92.9PE-0.1C-7.0Co	Vacuum about 10Pa
	4 93.0PG-7.0Co	Vacuum about 10Pa
	5 92.9PH-0.1C-7.0Co	Vacuum about 10Pa
	6 93.0PI-7.0Co	Vacuum about 10Pa
	7 92.8PJ-0.2C-7.0Co	Vacuum about 10Pa
	8 92.5PK-0.5Cr ₃ C ₂ -7.0Co	1 kPa Ar
	9 92.0PL-8.0Co	1 kPa Ar
	10 91.9PM-0.1C-8.0Co	1 kPa Ar
	11 90.0PO-2.0W-8.0Ni	10 kPa Ar
	12 89.0PP-3.0W-8.0Ni	10 kPa Ar
	13 92.0PQ-8.0Co	Vacuum about 10Pa
	14 91.8PR-0.2C-8.0Fe	1 kPa Ar
Comparative products	1 93.0CD-7.0Co	Vacuum about 10Pa
	2 62.5CA-30.0CB-0.5TiC-7.0Co	Vacuum about 10Pa
	3 92.2CA-0.8ZrC-7.0Co	Vacuum about 10Pa
	4 92.2CB-0.1C-0.7VC-7.0Co	Vacuum about 10Pa
	5 22.1CA-70.0CB-0.1C-0.8NbC-7.0Co	Vacuum about 10Pa
	6 82.2CA-10.0CB-0.8TaC-7.0Co	Vacuum about 10Pa
	7 90.0CH-1.6TaC-1.4TiC-7.0Co	Vacuum about 10Pa
	8 91.0CA-2.0Cr ₃ C ₂ -7.0Co	1 kPa Ar
	9 31.3CA-60.0CB-0.7Cr ₃ C ₂ -8.0Co	1 kPa Ar
	10 47.9CA-40.0CB-2.2W-0.4TaC-1.5Cr ₃ C ₂ -8.0Co	1 kPa Ar
	11 58.1CA-30.0CB-3.0W-0.9Mn-8.0Ni	10 kPa Ar
	12 48.0CA-40.0CB-3.0W-0.4TaC-0.6Mn-8.0Ni	10 kPa Ar
	13 91.1CH-0.9Re-8.0Co	Vacuum about 10Pa
	14 19.4CA-60.0CB-0.3C-0.5Cr ₃ C ₂ -1.8Re-8.0Fe	1 kPa Ar

The resulting hard alloy sample piece was subjected to wet polishing processing with a 230 mesh diamond whetstone to produce a sample with a size of 4.0 x 8.0 x 25.0 mm, and transverse-rupture strength (hereinafter abbreviated to as "TRS") was measured by the JIS method. Also, one surface of the same sample was subjected to lap processing with a diamond past having an average particle size of 0.3 μm , hardness and fracture toughness value K_{IC} (IM method) were measured under a load of 196N using a Vickers indenter.

Moreover, micro-structural photograph was taken by an electron microscope with regard to the lap surface of the respective samples, an average particle size of WC and contents of the binder phase and the cubic crystal compound were obtained by using an image treatment device. These results are shown in Table 5.

Table 5

Sam- ple No.		TRS (MPa)	Hard- ness (HV)	Fracture toughness value (MPa·m ^{1/2})	Parti- cle size of WC (μm)	Amount of binder phase (% by volume)	Amount of cubic crystal compound (% by volume)
Present products	1	3160	1640	11.6	3.1	11.8	0
	2	3050	1670	10.8	2.5	11.5	0.6(W,Ti)C
	3	2850	1660	11.3	3.0	11.6	0.2(Zr,W)C
	4	2770	1790	8.9	1.2	11.6	0.3VC
	5	3210	1710	10.7	1.8	11.6	0.2NbC
	6	3140	1650	11.1	2.7	11.7	0.1TaC
	7	2540	1680	10.0	3.4	11.1	4.7(W,Ti,Ta)C
	8	2910	1630	11.2	3.0	12.6	0
	9	2790	1650	10.5	1.9	13.6	0
	10	2780	1570	11.2	2.2	14.7	0
	11	2840	1610	10.9	2.3	13.7	0
	12	2920	1620	10.5	2.1	13.6	0
	13	2750	1620	10.6	3.2	13.5	0
	14	2790	1630	12.5	2.4	13.7	0
Comparative products	1	2530	1620	11.3	3.2	11.7	0.8(W,Ti)C
	2	2310	1640	10.5	2.5	11.5	2.9(W,Ti)C
	3	2420	1610	11.1	3.1	11.7	1.7(Zr,W)C
	4	2490	1770	8.8	1.2	11.6	1.9VC
	5	2170	1690	10.2	1.7	11.7	1.5NbC
	6	1980	1630	10.8	2.8	11.8	0.8TaC
	7	2410	1630	9.8	3.3	11.0	9.4(W,Ti,Ta)C
	8	2760	1590	10.9	3.0	15.1	0
	9	2650	1620	10.2	2.0	14.5	0
	10	2610	1530	10.7	2.5	15.8	0.5TaC
	11	2730	1590	10.5	2.3	15.0	0
	12	2840	1610	10.1	2.1	13.8	0.4TaC
	13	2750	1610	10.2	3.1	13.9	0
	14	2380	1600	12.0	2.3	14.7	0

The hard alloys produced by the W-based composite carbide

powder of the present invention are improved in all of hardness, strength, toughness, etc., as compared with the hard alloy using the conventional high purity WC, when the composition and the WC grain size are made almost the same, and for example, in the hard alloy to which a small amount of TiC or TaC is added, there is a remarkable effect that strength is highly improved.